Ammine(2,2'-bipyridine- κ^2N,N')-silver(I) nitrate: a dimer formed by π - π stacking and ligand-unsupported $\text{Ag} \cdots \text{Ag}$ interactions

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Reaction of AgNO_3 and 2,2'-bipyridine (bipy) under ultrasonic treatment gave the title compound, $[\text{Ag}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{NH}_3)]\text{NO}_3$. The crystal structure consists of dimers formed by two symmetry-related Ag^{I} -bipy monomers connected through intra-dimer π - π stacking and ligand-unsupported $\text{Ag} \cdots \text{Ag}$ interactions. A crystallographic C2 axis passes through the mid-point of and is perpendicular to the $\text{Ag} \cdots \text{Ag}^{\text{I}}(-x+1, y, -z+\frac{1}{2})$ axis. In addition, each Ag^{I} cation is coordinated by one chelating bipy ligand and one ammine ligand, giving a trigonal coordination environment capped by the symmetry-equivalent Ag atom. Molecules are assembled by $\text{Ag} \cdots \text{Ag}$, π - π , hydrogen-bond ($\text{N}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$) and weak $\text{Ag} \cdots \pi$ interactions into a three-dimensional framework. Comparing the products synthesized under different mechanical treatments, we found that reaction conditions have a significant influence on the resulting structures. The luminescence properties of the title compound are also discussed.

Comment

Self-assembled coordination structures are one of the most attractive areas of materials research due to their intriguing structural topologies and functional properties such as molecular adsorption, magnetism and luminescence (Biradha *et al.*, 2006; Wu *et al.*, 2009; Blake, Brooks *et al.*, 1999; Blake, Champness *et al.*, 1999; Evans & Lin, 2002; Kitagawa *et al.*, 2004; Yaghi *et al.*, 2003), and much attention has focused on their design and construction. However, the factors that govern the formation of such complexes are complicated and include not only the inherent properties of metal ions and ligand structure, but also anion-directed interactions and reaction conditions (Bu *et al.*, 2003; Kong *et al.*, 2008, 2009). In addition to covalent bonds, noncovalent interactions, such as

$\text{Ag} \cdots \text{Ag}$, π - π , hydrogen-bond and cation $\cdots \pi$ interactions, also play important roles in controlling molecular packing (Pedireddi *et al.*, 1996; Kolotuchin *et al.*, 1995; Li *et al.*, 2006; Sun *et al.*, 2003; Lough *et al.*, 2000; Massoud & Langer, 2009; Goodgame *et al.*, 2002). Because the central C—C bond of bipyridine (bipy) can rotate freely, bipy cannot just be regarded as a chelating ligand (Kaes *et al.*, 2000; Marchetti *et al.*, 2007), but also as a potential spacer between metal centers by acting as a bridging ligand with an *anti* configuration (Yu *et al.*, 2007; Forniés *et al.*, 1993). Therefore, bipy and its derivatives are widely used in the construction of novel Ag^{I} -containing complexes incorporating diverse supramolecular interactions (Hung-Low *et al.*, 2009; Ye *et al.*, 2005). Recently, we have pursued systematic investigations into the assembly of Ag^{I} cations with different angular and linear bipodal *N*-donor ligands, such as aminopyrimidine and aminopyrazine (e.g. Luo, Huang, Chen *et al.*, 2008; Luo, Huang, Zhang *et al.*, 2008; Luo *et al.*, 2009; Sun, Luo, Huang *et al.*, 2009; Sun, Luo, Xu *et al.*, 2009; Sun, Luo, Zhang *et al.*, 2009), with the principal aim of obtaining supramolecular complexes or multifunctional coordination polymers. In an attempt to exploit the influence of synthesis conditions on the structures of the AgNO_3 -bipy system, we successfully obtained the title compound, (I), and the known coordination polymer, (II) [*catena*-poly{[(2,2'-bipyridine)silver(I)]- μ_2 -nitrate}]; Bowmaker *et al.*, 2005}, in the same solvent system.

The asymmetric unit of (I) contains one Ag^{I} cation, one bipy ligand, one coordinated ammonia molecule and one nitrate anion. As shown in Fig. 1, the Ag^{I} cation is coordinated in a trigonal-planar fashion by three N atoms from one bipy ligand and one ammonia molecule, with bond angles ranging from 72.36 (12) to 145.25 (14)°. The $\text{Ag}-\text{N}_{\text{bipy}}$ bond lengths are identical within experimental error (Table 1) and comparable to reported values (Oxtoby *et al.*, 2002; Fan *et al.*, 2007; Nicola *et al.*, 2007). The pyridyl rings of bipy are nearly coplanar with a twist angle of 4.8 (5)°. With an $\text{Ag}-\text{N}$ bond length of 2.135 (4) Å, the coordinated ammonia molecule plays a role as terminator, obstructing aggregation of (I). Because of the labile nature of this $\text{Ag}-\text{N}$ bond, the presence of ammonia in the coordination sphere of the metal center offers a potential coordination site in the molecule. Two symmetry-related Ag^{I} -bipy monomers aggregate to a dimer with a head-to-head arrangement through intra-dimer π - π stacking and a ligand-unsupported $\text{Ag} \cdots \text{Ag}$ interaction (Tong *et al.*, 1999), where the $\text{Ag}^{\text{I}} \cdots \text{Ag}^{\text{I}}$ interaction [symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$] has a distance of 3.0456 (16) Å. This is significantly shorter than twice the van der Waals radius of Ag^{I} (3.44 Å; Bondi, 1964) and the completed coordination sphere of the Ag centers can thus be described as capped

Figure 1

The structure of (I), showing the atom-numbering scheme and the coordination environment around the Ag^{I} centre. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

Figure 2

A ball-stick perspective view of the π - π stacking (green dashed lines in the electronic version of the paper) between the pyridyl rings of neighboring bipy ligands and the $\text{Ag}\cdots\text{Ag}$ interactions (golden dashed lines). H atoms and nitrate anions have been omitted for clarity.

trigonal planar. The other cases where such short contacts exist between nonbridged Ag^{I} cations are found in $\text{Ag}(\text{imidazole})_2\text{ClO}_4$ (Eastland *et al.*, 1980) and $[\text{Cu}(\text{ethylenediamine})_3][\text{Ag}_2(\text{CN})_4]$ (Kappenstein *et al.*, 1988). A crystallographic C2 axis passes through the mid-point of and is perpendicular to this $\text{Ag1}\cdots\text{Ag1}^{\text{i}}$ axis. This weak bonding interaction between two d^{10} cations is possible *via* the participation of 5s and 5p orbitals which are close in energy to the 4d orbitals. Intra-dimer π - π stacking also contributes to the reinforcement of this $\text{Ag}\cdots\text{Ag}$ interaction (Venkatalakshmi *et al.*, 1992). Moreover, the π - π stacking [$\text{Cg1}\cdots\text{Cg2}^{\text{i}} = 3.628(3) \text{ \AA}$ (intra-dimer) and $\text{Cg1}\cdots\text{Cg2}^{\text{vi}} = 3.711(3) \text{ \AA}$ (inter-dimer); Cg1 and Cg2 are the centroids of the N1/C1-C5 and N2/C6-C10 rings, respectively; symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (vi) $-x + 1, -y + 1, -z$; Fig. 2] and weak $\text{Ag}\cdots\text{C}$ interactions [$\text{Ag1}\cdots\text{C6}^{\text{vi}} = 3.386(4) \text{ \AA}$ and $\text{Ag1}\cdots\text{C7}^{\text{vi}} = 3.393(5) \text{ \AA}$] act as a 'glue' to reinforce the dimers, forming a column along the *c* axis, in which the dimers are arranged in a head-to-tail orientation. In addition, the nitrate anion acts as an acceptor and is hydrogen bonded to

Figure 3

A ball-stick perspective view of the three-dimensional supramolecular framework incorporating hydrogen bonds (dashed lines).

Figure 4

Photoluminescence spectrum of (I) (solid line) and free bipy (dotted line) in the solid state.

three different symmetry equivalents of the ammonia molecules (Table 2). Nonclassical $\text{C}_{\text{pyridyl}}\cdots\text{H}\cdots\text{O}$ hydrogen bonds [average $\text{C}\cdots\text{O}$ distance = $3.280(5) \text{ \AA}$; Table 2] and classical $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds link adjacent columns to form the resulting three-dimensional supramolecular framework (Fig. 3).

The effects of the synthesis conditions on the structure of the AgNO_3 -bipy system were investigated in the ultrasonic and stirred methods with the same solvent system (methanol-water; 15 ml, 1:2 v/v). Under stirring, we could only obtain coordination polymer (II), first reported by Bowmaker *et al.* (2005). In the structure of (II), the nitrate anion not only acts as a ligand but also as a bridging anion to link Ag^{I} -bipy cationic units into one-dimensional zigzag chains. The difference between the structures of (I) and (II) originates mainly from the different mechanical treatments which cause the

ammonia molecule and nitrate anion to play different roles in the construction of (I) and (II).

It is known that the free bipy molecule displays a weak luminescence at *circa* 530 nm in the solid state at room temperature. As shown in Fig. 4, compound (I) exhibits an intense emission maximum at 469 nm upon excitation at 345 nm, which may be attributed to the intraligand emission from bipy (Wang *et al.*, 2004). Compared with that of the free bipy molecule, the blue shift and the luminescent enhancement of the emission at 469 nm may be due to the chelation of the bipy ligand to the Ag^I cation, which effectively increases the rigidity and coplanarity of the ligand and reduces the loss of energy by nonradiative decay of the intraligand emission excited state (Zhang *et al.*, 2003; Qian & Wang, 2002).

Experimental

All reagents and solvents were used as obtained commercially without further purification. A mixture of AgNO₃ (170 mg, 1 mmol) and 2,2'-bipyridine (156 mg, 1 mmol) was added to a methanol–water solvent mixture (15 ml, 1:2 v/v) under ultrasonic conditions, which helped to dissolve the white precipitate. An aqueous NH₃ solution (25%) was added dropwise to the mixture to give a clear solution. The resulting solution was left to evaporate slowly in the dark at room temperature for several weeks to give crystals of (I) in the form of yellow prisms. The crystals were washed with deionized water and dried in air (yield *ca* 51%, based on Ag). Analysis calculated for C₂₀H₂₂Ag₂N₈O₆: C 35.01, H 3.23, N 16.33%; found: C 34.95, H 3.14, N 16.27%.

Crystal data

[Ag(C ₁₀ H ₈ N ₂)(NH ₃)]NO ₃	<i>V</i> = 2403 (2) Å ³
<i>M_r</i> = 343.10	<i>Z</i> = 8
Monoclinic, <i>C</i> 2/ <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 17.685 (9) Å	<i>μ</i> = 1.68 mm ^{−1}
<i>b</i> = 10.690 (5) Å	<i>T</i> = 298 K
<i>c</i> = 12.748 (7) Å	0.10 × 0.08 × 0.08 mm
<i>β</i> = 94.457 (12)°	

Data collection

Oxford Diffraction Gemini S Ultra diffractometer	4406 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	2320 independent reflections
<i>T_{min}</i> = 0.850, <i>T_{max}</i> = 0.877	2161 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.030

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.044	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.112	<i>Δρ_{max}</i> = 0.85 e Å ^{−3}
<i>S</i> = 1.21	<i>Δρ_{min}</i> = −0.59 e Å ^{−3}
2320 reflections	
172 parameters	
6 restraints	

The aromatic H atoms were generated geometrically (C–H = 0.93 Å) and allowed to ride on their parent atoms in the riding-model approximation, with *U_{iso}*(H) = 1.2*U_{eq}*(C). The positions of the ammonia H atoms were located from difference maps and refined with the N–H distances restrained to 0.89 (2) Å, the H···H distances restrained to be similar with a tolerance s.u. of 0.04 Å and with *U_{iso}*(H) = 1.5*U_{eq}*(N).

Table 1

Selected geometric parameters (Å, °).

Ag1–N3	2.135 (4)	Ag1–N1	2.302 (3)
Ag1–N2	2.296 (3)	Ag1–Ag1 ⁱ	3.0456 (16)
N3–Ag1–N2	142.34 (14)	N3–Ag1–Ag1 ⁱ	93.86 (11)
N3–Ag1–N1	145.25 (14)	N2–Ag1–Ag1 ⁱ	100.92 (8)
N2–Ag1–N1	72.36 (12)	N1–Ag1–Ag1 ⁱ	75.91 (8)

Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N3–H3A···O1 ⁱⁱ	0.87 (2)	2.14 (2)	2.998 (6)	170 (5)
N3–H3B···O3 ⁱⁱⁱ	0.89 (2)	2.23 (2)	3.110 (5)	169 (4)
N3–H3C···O2 ^{iv}	0.88 (2)	2.30 (2)	3.177 (5)	172 (5)
C1–H1···O3 ⁱⁱ	0.93	2.39	3.307 (5)	169
C7–H7···O1 ^v	0.93	2.27	3.192 (5)	169
C10–H10···O2 ⁱ	0.93	2.58	3.340 (6)	139

Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (v) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008) and *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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